Hybrid Sol-gel Coatings Produced from TEOS and γ-MPS

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The aim of this work was to prepare coatings onto glass slides from polymeric sols. Hybrids sols from tetraetoxysilane (TEOS) and 3-(metacryloxypropil)trimethoxysilane (γ-MPS) were prepared in acid medium for different TEOS/γ-MPS ratios and they were modified by the addition of a colloidal silica suspension and/or titanium alcoxyde. The stability of the different sols was evaluated by viscosity measurements; the sols showed a Newtonian behaviour and the ageing effect is negligible even after two months from their preparation. Coatings were obtained by dipping at different withdrawal rates and heat-treated between 150 and 250ºC. The thickness of the coatings was measured by profilometry and their thermal stability was followed by TGA-DTA. The thermal analysis allows determining the limit temperatures at which the coatings can be treated without loss its hybrid character. Transparent coatings with thickness higher than 4 μm were reached for most of the studied compositions .

1. INTRODUCTION

Sol-gel method is a simple technique used to produce adherent and crack-free silica coatings, whose most important feature consists on the low sintering temperatures [1,2]. In the last years, hybrid organic-inorganic coatings have been developed in order to improve mechanical, optical and abrasion properties [3,4,5]. Trifunctional alkoxysilanes $R'Si(OR)_3$, where R and R´ are alkyls groups, have been used as starting materials to introduce organic groups in the coatings. The reactive organic groups present in the alkyl chains, as vinyls and methacryls groups, can react at low temperature producing crosslinked polymeric networks. One of the trialcoxysilane usually employed for this purpose is the 3-(methacryloxypropyl)trimethoxisilane (γ-MPS). Recently, hybrid coatings and bulk materials have been obtained from the hydrolysis and condensation of γ-MPS, the microhardness of these coatings being lower than that of glass slides [6].

The aim of this work was to obtain hybrid inorganic-organic coatings from TEOS and γ-MPS, modified by adding different molar ratios of titanium isopropoxyde and a colloidal silica suspension in order to increase the hardness and scratch resistance.

2. EXPERIMENTAL

Three different solutions were prepared. The first silica solution (S) was obtained from tetraethoxysilane (TEOS), 3-(methacryloxypropyl)trimethoxysilane (γ-MPS) by adding diluted HNO_3 (0.1 N) to produce hydrolysis and condensation reactions. The molar ratios $H_2O/(TEOS+\gamma\text{-MPS})$ were changed between 3.9 – 3.25. Initial sols were diluted with absolute ethanol up to a silica concentration of 150 g/l.

Another silica suspension (C) was prepared mixing TEOS, γ-MPS and a colloidal suspension of silica (Levasil 200A, Bayer, Germany, particle size 15nm, and pH 9). Concentrated HNO_3 was used as catalyst to reach a pH between 2 - 3. The molar ratio TEOS/γ-MPS was equal to 1, the final silica concentration of 250 g/l being got by diluting with a mixture of ispropyl/butylglycol.

A third solution (T) was obtained by incorporating titanium isopropoxide (TTi). First, TEOS and (γ-MPS) were pre-hydrolysed during 30 minutes at room temperature by addition of half of the total water necessary to complete the hydrolysis. On the other hand, the titanium alcoxide was modified with acetyl acetone and later mixed with the first solution before adding the rest of the water. The molar ratio TEOS/TTi was fixed to 1.5 and the molar ratios γ-MPS/(TEOS+TTi) to 0.1 and 0.5.

Table 1 shows the molar ratios of TEOS, γ-MPS, TTi and the colloidal silica for each studied solutions.

Table 1. Compositions of the sols

Synthesis	TEOS	γ-MPS	TTi	Colloidal SiO_2
S1	90	10		
S2	75	25		
S3	50	50		
S4	25	75		
C1	30	30		40
C2	20	20		60
C3	15	15		70
T1	54	10	36	
T2	30	50	20	

The stability of the sols was studied through viscosity, using a rheometer (Haake, RS50, Germany) under controlled rate conditions at 25ºC.

Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were performed on bulk gelled at 60°C from the series S. These analyses were carried out at a heating rate of 10°C/min up to 500°C in air, using a Netzsch (Simultaneous Thermal Analysis STA 409) equipment. Self-supported layers were produced by gelling at 60°C with the S series and tested by TGA using the same conditions. Isothermal TGA was also performed to simulate curing conditions, at two temperature, 150 and 250°C for 1 hour.

Coatings were obtained on glass slides by dip-coating at a withdrawal rate between 10 and 52 cm/min to get the critical thickness corresponding to each sol. The films were dried at room temperature and densified during 30 minutes at temperatures between 100°C and 300°C with a heating rate of 10°C/min in air. The thickness of the coatings was measured by profilometry (Talystep, UK).

3. RESULTS AND DISCUSSION

The sols were characterised by determining viscosity changes with the ageing time. All the sols showed a Newtonian behaviour, maintained for at least nine weeks without important changes. When nanoparticles are added to sol, the stability is still high although the viscosity slightly increases from 3.5 mPa.s for the sol S to 5 mPa.s for sol C.

Figure 1 shows the thermo gravimetric curves of films gelled at 60°C. The curves show that the higher the organic concentration in the samples the higher is the degradation rate.

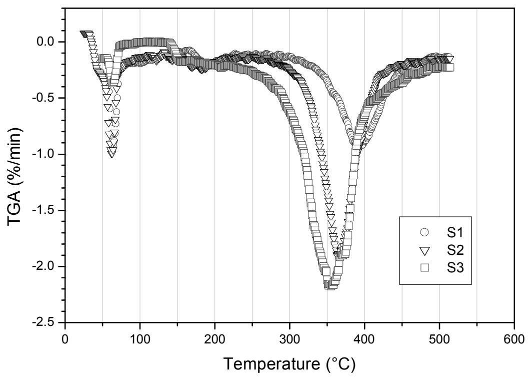

Figure 1. TGA curves as a function of temperature

The TGA and DTA tests were also performed with bulk gelled samples using the same test parameters. The results show a similar trend, although the temperatures of degradation of organic groups take place at lower temperatures, probably due to the lower porosity exhibited for the films compared with that obtained for the bulk sample. The rate of degradation is faster with increasing porosity due to greater oxygen diffusion. Thus, gas diffusion and oxidation of the organic species in the bulk porous material is favoured.

On other hand, isothermal TGA at 150 and 250°C were performed on self-supported gelled films. Figure 2 shows isothermal TGA tests at 150°C of films from S series. The first part of the curves corresponds to water and alcohol losses. Since the hydrophobic character of the material increases with increasing γ–MPS contents the mass loss is lower for higher organic contents. On the other hand, in the test performed at 250ºC, two different sections are observed. The first is also due to loss of water and alcohol, and the second is produced by thermal degradation of the organic species present in the γ-MPS.

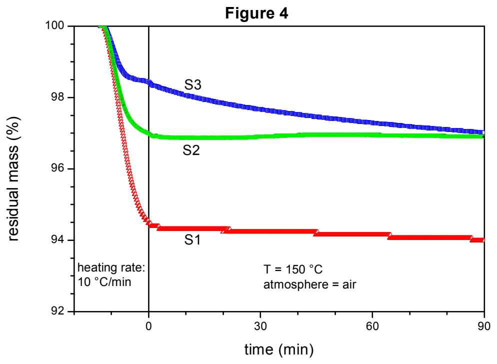

Figure 2. Isothermal TGA curves as a function of time from compositions S

Coatings onto slide-glass were prepared at different withdrawals rates and cured between 100 and 300ºC. The critical thickness decreases with increasing densification temperature. Figure 3 shows the evolution of the critical thickness for S compositions as a function of densification temperature.

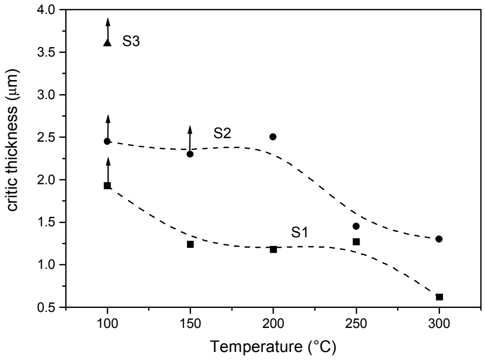

Figure 3. Critical thickness as a function of densification temperature for S compositions

Coatings obtained from sol S3, thermally treated at 150°C, C1 and C2 thermally treated at 250°C, and S4 with every thermal treatment, exhibit lack of homogeneity presenting waves or drips. These dripping phenomenons may be caused by the presence of γ-MPS as reagent. When the organic fraction is higher than 40% drying at room temperature is not totally effective. When samples are subjected to thermal treatments, the film viscosity reduces and the film flows producing the dripping phenomenon. In order to avoid this behaviour, a pre-curing step at lower temperature and/or the addition of a curing agent to avoid plastic flow is suggested.

Coatings obtained from T1 sol, containing titanium isopropoxide, showed lower critical thickness. On the contrary, the critical thickness was not reached in γ-MPS-rich coatings obtained from T2 sols. These coatings showed high homogeneity and good appearance. The use of Ti-containing reagent in the synthesis of T1 and T2 sols favoured the disappearing of dripping in the obtained coatings.

Since $\mathbf{e} \propto \mathbf{v}^n$, where **e** is the coating thickness in µm, and **v** is the withdrawal rate in cm/min; n was calculated by least-squares regression. The obtained values vary between 0.79 and 0.87 for each composition and thermal treatment, while the deduced value by I. Strawbridge et al.[7] and Guglielmi et al.[8] for inorganic coatings is 0.5. Deviations in this slope are attributed to the rheological and flowing behaviour of the sols and the singular hybrid structure of coatings obtained from γ-MPS, although this effect must be further studied for total clarifying.

4. CONCLUSIONS

The hybrid sols prepared from TEOS and γ-MPS show a Newtonian behaviour, ageing effect being negligible even after two months of storage.

The limit temperature for coating densification decreases with γ-MPS content, and it should be always lower than 200ºC for S1 sols and 180ºC and 150ºC for S2 and S3 sols respectively.

γ-MPS contents higher than 40% produce non-smooth coatings surfaces due to viscoplastic behaviour. In order to avoid this phenomenon, a pre-curing step at lower temperature and/or the addition of a curing agent to avoid plastic flow is suggested.

The addition of γ-MPS produces a strong increase in the coating critical thickness. Furthermore, it strongly increases the value of n (a parameter which relates the coating thickness with the withdrawal rate), from 0.5 (in non-containing g-MPS sols) to 0.79 - 0.87, depending on γ-MPS content.

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